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New Class of Apparatus for Crystal Growth from Melt

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1. Introduction

In this chapter, we offer original solutions for crystallization devices by presenting a set of cooling devices that are upgraded models of the existing ones used in a well-known apparatus for crystal growth. Many basic ideas from these articles were used as a starting point for the creation of the new, modern multifunctional devices that may be used both as standard school laboratory tool and as industrial equipment. A number of crystal growth devices previously employed were designed to match contemporary technology level and needs for specific monocrystal growth. This led to the additional engagement on the realization of new working conditions, thereby increasing production costs. In light of this problem, while developing new forms of crystal growth apparatus we also have aimed at making the whole process as economical [1], approachable and efficient as possible.

A brief review of twentieth century devices for the crystal growth from the melt [2, 3, 4] reveals widely accepted remarks on some not so good characteristics of specific apparatus components. Let's mention Tamman's test tube and its tip modification which is essential to the crystal germ formation, realization of suitable apparatus geometry, construction of cooler parts in order to have controlled under-cooling, some specific demands for the adequate temperature gradient. Within this chapter, we have defined certain activities conducted (with the set goal in mind) in order to improve existing and to develop new crystal growth devices. We started with a set of simple steps that allowed for the modeling and construction of school type apparatus [5, 6, 7]. Later on, we came up with original solutions and more complex devices with a number of advantages compared to the known crystal growth devices.

Construction of new devices has as its ultimate goal apparatus standardization. Therefore, in a number of papers we have performed calculations that justify the use of newly designed apparatus. As a matter of fact, in previous research, a standard and widely used approach in technology of crystal growth was to make a specific prototype of apparatus, and then, through a variety of experimentally gained data, to upgrade and improve the characteristics of crystal growth process, depending on the specific demand set for the purpose [2, 3]. That kind of approach was uneconomical regarding time consumption, and a large number of unsuccessful attempts was something one had to count on. For each specific demand a construction of an apparatus almost identical (with a slight modification only) to the one that failed was necessary. In turn, this led to significant material investments for the

research, therefore making the crystal growth research a privilege of financially powerful countries that had the opportunity of gathering the top quality researchers from all over the world. Nevertheless, such huge investments had its justification in the fact that some extraordinary results were achieved. This resulted in production of materials of exceptional purity, as well of some new substances and materials whose crystals were realized for the first time in laboratory conditions.

These new materials found its immediate application in the military industry, where high quality materials are imperative, but also in some industrial branches, making these countries top producers of relevant materials (revolutionary novelties in semiconductor technology, telecommunication and optical devices).

Modern apparatus and its modifications presented here have common characteristics of not being financially [1] demanding (starting with the simple to the complex ones). Secondly, it is desirable to have apparatus that will allow for the large number of repetitions of similar processes (with small modifications only and development of new simple parts of equipment for possible improvements of crystal growth conditions). We went even further by developing models and constructing the devices with suitable geometry that allow for the crystallization of a single substance with different crystallization rates and temperature gradients. In addition, it is possible to achieve crystallization of different materials within the single event by employing materials with similar melting points, while having different crystallization rates and temperature gradients.

Along with previously stated advantages of developed apparatuses, we attempted and applied numerical calculations (whenever possible) to get best possible set of parameters in preparation of a new model for crystallization processes. One such analysis takes into account the dimensions of apparatus parts as well as interrelations among the most relevant crystallization factors that will allow for the optimal quality final product – crystal or monocrystal.

In general, intention of the authors is to intertwine these modern devices (large repeatability and multifunctional aspect of crystallization process being the most important advantages) with relevant numerical calculations and existing software. Computer regulated and monitored crystallization would give us more insight on how different parameter variation (such as temperature variations, heat transfer, crystallization rate etc.) and different apparatus dimensions, influences the crystallization process. In other words, there is a tendency to perform all the possible calculations in order to take necessary steps to modify and improve crystallization, so that we would get a crystal of predefined characteristics in a modern and efficient way by using state-of the-art information technologies within the regime of so-called expert systems.

2. New classes of coolers

In accordance with plans based on the variety of possible choices of data on architecture, construction and reconstruction of crystallization apparatus, we came upon a number of creative ideas that are directed towards the adaptations of apparatus shape within the laboratory conditions, the form of coolers and its more efficient role in crystallization apparatus. Long time experience based on the years of the research led author to the conclusion that the heat conduction is one of the essential factors determining the crystallization rate. When, in the conditions of undercooling, the heat is being released, the undercooling will exist only if the heat is being taken away in a proper manner. The

rate of heat conduction is a factor quite responsible for the crystallization rate. Crystal growth rate is constant when there is a balance in heat transfer. The heat transfer is quite a complex problem in the sense of regulating the system that has a continuous and controlled operation in accordance with the predefined phases of the crystallization process. From the very start of the germ formation, it is necessary to get a desired temperature drop that defines the initial state of crystallization, and then, by setting an appropriate temperature gradient one can have optimal conditions for obtaining the crystal of specific characteristics.

The temperature aspect of the crystallization that is so significant for the crystal growth and possibility of programming the process parameters through various shapes and positioning of the coolers (which provide cold fluid flow in crystallization apparatus), demands coolers to have multiple roles: firstly, to enable for more precise crystallization, and secondly, to lead to construction of new coolers made of materials of adequate heat conductivity so to have more convenient conditions for crystal growth from the melt.

Besides, suitably designed coolers have such a shape that they may simultaneously serve as ampoule carriers or test tubes with melt. In this way, the crystallization will be easily controlled. When looking back at the devices previously used, it is easy to see that some parts of the devices were burdened by carriers of pots with melt, as well as due to their heating and operating them in and out of the apparatus. Also, realization of adequate temperature gradient and subcooling through complicated pipe constructions or other forms of the coolers of intricate geometries (positioned within the crystallization apparatus), additionally complicated crystallization apparatus, not to mention the other instruments used in the process. Detailed analysis of these problems gave us very useful data that generated a completely new set of ideas, which ultimately resulted in a new, more complex role that coolers have in process. Their multifunctionality led to significant simplification in apparatus construction in many of the known methods, which, loosely speaking, were reinvented. In some of author's papers, a demand for cooler improvement was set, and it resulted in design of more efficient and modern generation of crystallization devices.

As a basis for the design of novel or significantly improved and modified standard crystallization devices, we have used a series of originally, for the purpose-constructed coolers presented within the chapter. Cooler models presented in Figs 1- 6, whose forms and functionality gained recognition through presentation in few articles, may be divided in several groups, based on its positioning in the apparatus, cooling fluid flow propagation and its intended method application (Tamman, Stober, Czochralski). The general classification, which arises from the position of the cooler within the apparatus, leads us to two types of coolers: vertical and horizontal.

2.1 Vertical air coolers

Coolers where the cooled air is moving along defined (vertical) tube direction, belong to the group of so called vertical air coolers (Fig. 1). Thanks to the different cross sections of the tube, different speeds of airflow are possible. In that way, various crystallization speeds via heat dissipation are established in test tubes that are attached to the body of the cooler in various manners. There is a whole spectrum of coolers based on the positioning of the test tubes: the ones with fixed test tube position, to the ones with mobile rings on mobile coolers. Large number of test tube positions is available (Fig. 3).

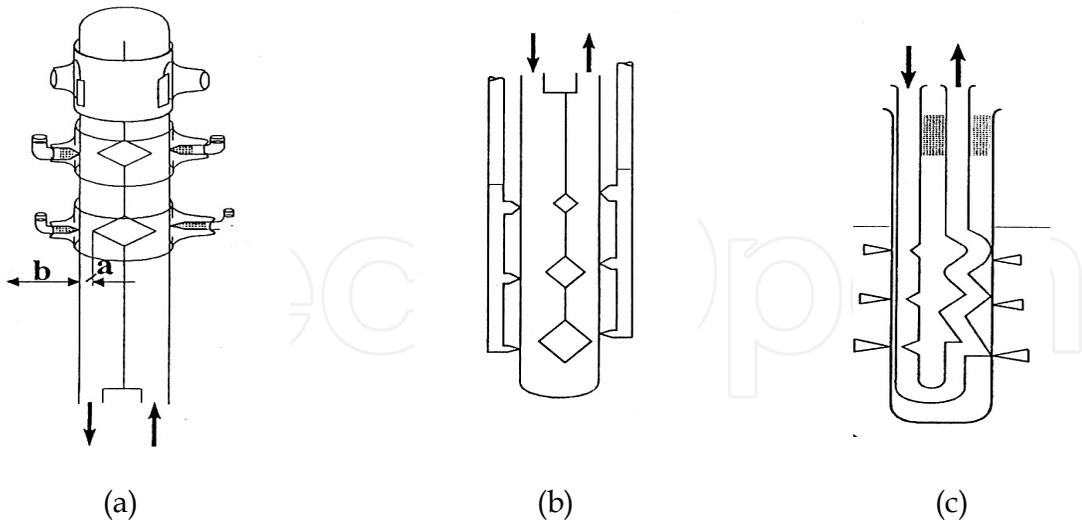


Fig. 1. Vertical coolers: (a) cold "finger", (b) "cold key" and (c) "cold ear-rings".

For the class of coolers presented in Fig. 2, the line of development was the following one: in certain positions, the tubes were constricted and slightly bended, so to achieve the optimal heat dissipation, and to simultaneously allow for an additional number of test tubes to be positioned. This was followed by coolers where the pipes were ring like bended in a couple of independent levels of crucibles, which allows for an increase in crucible operating capacity.

The operating regime of this class of coolers is such that each ring has a direct fluid flow within it and heat dissipation in the environment. The other opportunity are so called spiral coolers where heat generated during the crystallization process from all the rings is being "collected" and dissipated into environment. Detailed analysis of presented models showed some additional possibilities of vertical coolers. These were used for some novel practical solutions. Depending on the geometry of the space the coolers are in, they may be maneuvered (so called movable vertical air coolers) or be fixed while some of the other pipes (with Tamman test tubes) can be maneuvered on order to get a desired temperature gradient or crystallization rate. Whenever the vertical air coolers are employed, whether its orientation is upside down or vice versa, fluid flow is such that it returns in the opposite direction along the same path.

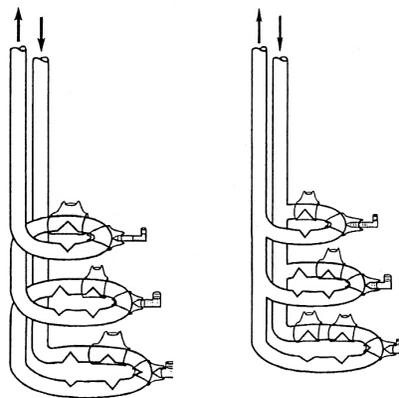


Fig. 2. Air cooler model ("crystallization spiral").

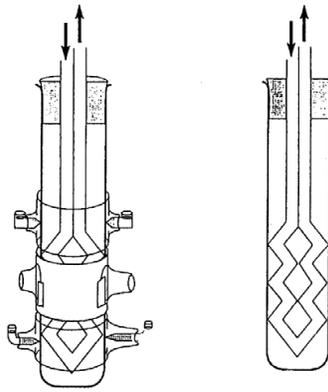


Fig. 3. Air cooler model ("crystallization key").

2.2 Horizontal air coolers

When talking about the horizontal air coolers, there are, basically, two classes with some specific variations:

- To the first group belong coolers whose fluid flow pipes are horizontal. The cold fluid enters on one side and exits on the other one (single pipe horizontal air cooler, Fig. 4; system may also have two or more horizontal pipes). Couple of horizontal coolers can form an ensemble of instruments in chamber or crucible furnace.
- Other type of cooler employed in the crystallization purposes, is the one where a horizontal pipe is bended at its end, carrying the fluid in the direction opposite to the initial one, and then the heat is being dissipated into environment (Fig. 4b. and Fig. 5.). If the pipe is bended at 180° , there is a possibility of multiplying initial activities via new conditions and test tube positioning. This allows for a large interval of crystallization rates in direction of the cooler.

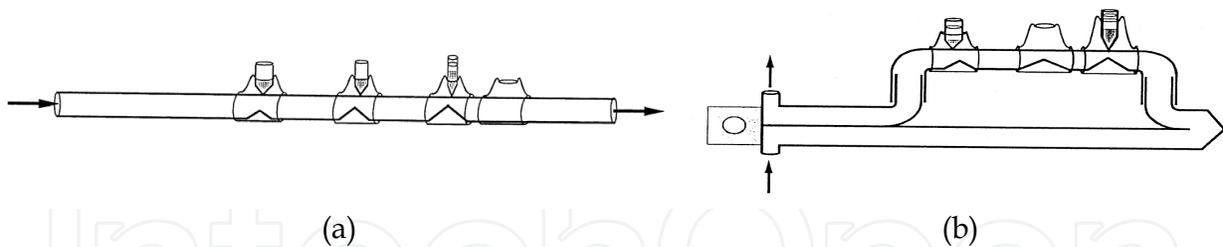


Fig. 4. Horizontal coolers: (a) pipe, (b) two-pipe (folding)

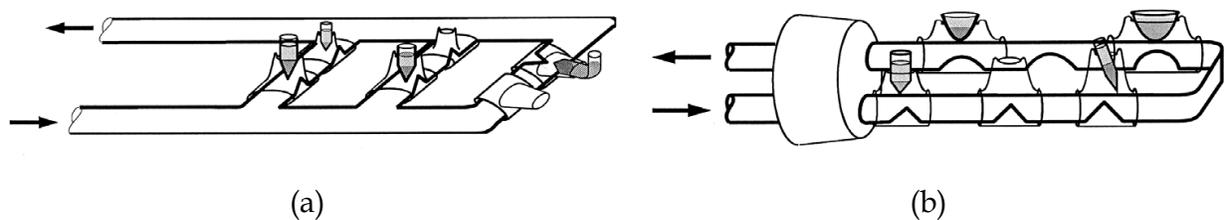


Fig. 5. Multifunctional horizontal coolers: a) the standard method, b) for the combined methods.

In such cases, we have come up with an original solution. The flow that convects heat below Tamman's test tubes is now being used for cooling the top layer of the melt that is positioned next to the exit pipes of the cooler. In that way, we have assigned it a new role upon bending the initial pipe. It gives us the opportunity of constructing the apparatus with new combined methods (Tamman's and Stober's). In Fig. 5, we present two solutions from a whole family of coolers whose realization is based on previously presented idea that leads to greater operability and more economical functioning in the crystallization process. Solutions presented give a clearly confirm validity of idea of redesigning some parts of cooler as well apparatus as a whole, and undoubtedly point out their versatile practical purposes.

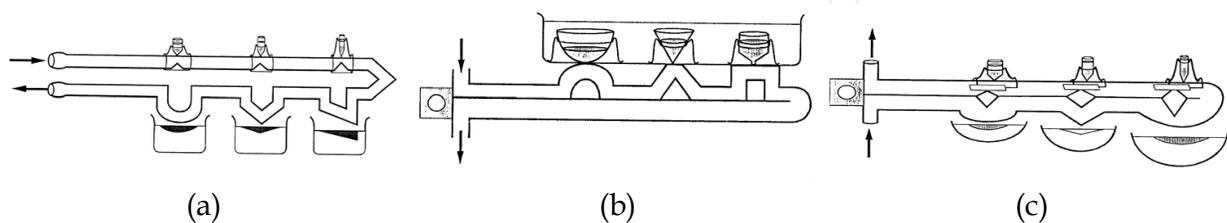


Fig. 6. Horizontal coolers; modification (a) and (c) combined with multivariate methods (b) variation of a method.

In Fig.6, specific horizontal coolers are given. Some parts of pipes are bended in the outer part of the device (unlike the previous ones where constrictions exist on the inner parts only) having endings of different geometrical shapes that allow different flow velocities. We have therefore met the conditions necessary for Stober method crystallization.

In this way, in the course of a single event, we have enabled crystallization based on the two methods, one during the fluid flow in the one direction, and the other for the opposite direction flow. In one case the cooling fluid flows above the crucibles containing crystallization melt. In the other, the flow goes below the melt where, by under-cooling specific capillary endings of test tubes with melt, a new process of germ creation starts all the way to the final crystallization. A geometrical representation of such coolers reminds of "cold horseshoes" and "cold keys". Fig. 11 demonstrates application of the modified cooler, which comprises two horizontal pipes mutually joined to movable pipe, which is an exceptional improvement compared to former examples in a sense of simplified geometry modification and crystallization conditions.

In some of horizontal coolers with one or more pipes containing cold fluid, another innovation is present. The pipe of cooler is introduced into a pipe of greater diameter, which may consist of one or two parts (Fig. 10) with small openings and slots, in which the position of pots and test tubes with melt may be fixed. Such a solution has clear advantages to the previously described ones, since by simply moving the cylindrical pipe (whose function is to move the cooler pipe and to serve as a test tube carrier all at once) a large number of different crystallization conditions and new crystallization geometries is achieved.

3. Original crystallization apparatus

The installation of the innovated systems for cooling, with the aim to monitor heat removal for the regulations of the processes of crystal growth from melted materials, enabled

obtaining more devices for crystallization. The new classes of cooling devices, with aforementioned advantages linked to the crystallization processes have an additional quality which is that those cooling devices are very adaptive for installation and operative by application in well known laboratories-crucibles, chamber furnaces and tube furnaces. However, more complex cooling systems with the Tamman's test tubes, as a carriers devices, need to create new forms of crystallization apparatuses. The projecting of the new classes of devices for crystal growth of melts, which will be shown in the following text, is the response to the aforementioned need.

From these methods for crystal growth from the melt, it is estimated that in the school laboratory, the Tamman's method is the most convenient one. If we use the advantages of the horizontal single tube aerial cooling system, an original device, the so called "crystallization bench" can be realized [8]. It consists of a tube furnace and a specially adapted cooling system (Fig 7.).

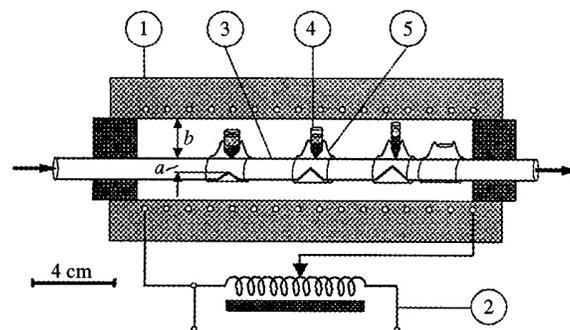


Fig. 7. Crystallization regulation in a tube furnace. (1) electroresistant tube furnace, (2) continuously changeable transformer, (3) air cooler ("cold bench"), (4) Tamman test tubes and (5) rings.

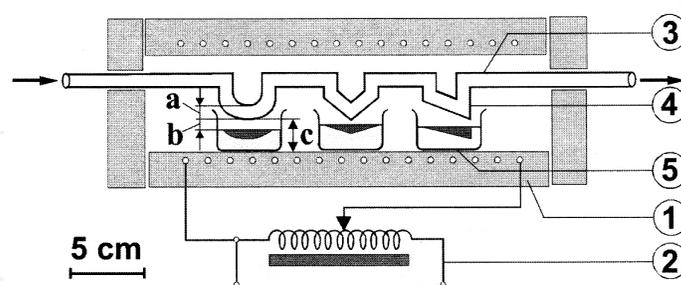


Fig. 8. A chamber furnace for obtaining crystals. (1) laboratory chamber furnace, (2) continuously changeable transformer, (3) air cooler ("cold key"), (4) cold "teeth" (5) crucibles with the floating crystals.

The procedure of choosing the wanted disposition of the test tubes, with the melted material, above the narrowing cooler cross section, is accomplished with moving rings on the cooler tubes. The devices may contain many Tamman's test tubes of various sizes and dispositions. The constructed device enables the simultaneous test of a few various nucleation and crystallization rates. Tamman test tubes of various shapes and dimensions (a family group [2, 3, 4] can be mounted on the test tube rings and thus simultaneously tested).

The variations considering the disposition changes of certain test tubes, as well as simultaneous regulations of some temperature gradients are also possible. The working regime of the devices works as following: at a constant furnace temperature, a weak air flow is turned on through the cooler. There, the crystallization starts on the bottom of the test tube (Fig.9).

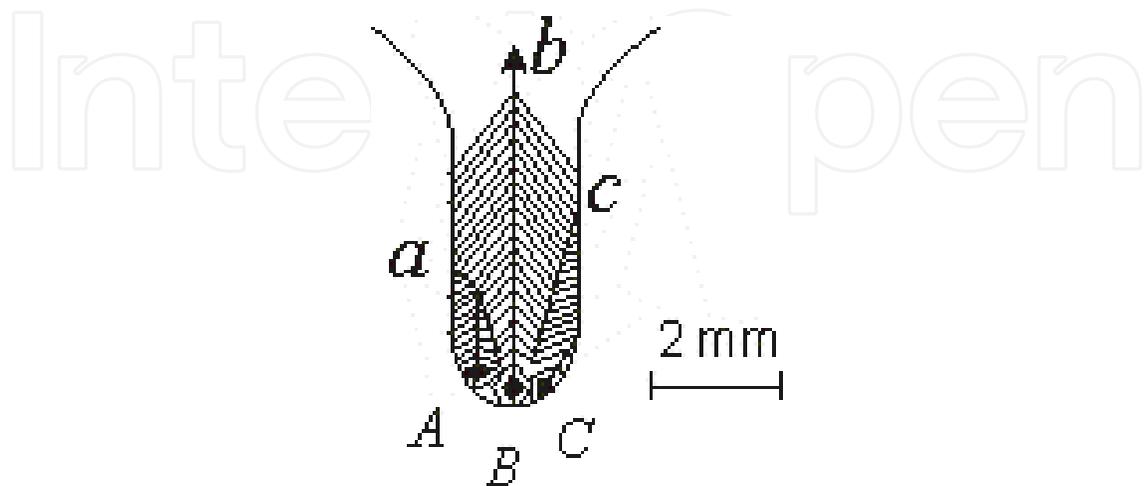


Fig. 9. The beginning of the crystallization at the bottom of the capillary tube.

The bottom of the test tube continues in the capillary, so that in the beginning of the process, only a small amount of the melt is overcooled. Therefore, only certain crystal nucleuses can be formed. The nucleation which grows towards the walls of the capillary, stop growing at a certain time. Only the nucleation which grows towards the axis of the capillary overgrows the other nucleations, and when they exit the capillaries, they expand to the full cross section of the testing tube.

The preparation of crystals of good quality, containing a low concentration of impurities and defects, requires a crystallizable substance of high purity, test tubes of materials that do not react chemically with the melt, a high degree of temperature stabilization of the furnace, and the absence of shocks [9]. The conditions required to grow crystals of some example substances, which have low melting temperatures and can be used to obtain single crystals in school laboratory.

The crystallization rate interval [4] in each tube is regulated by the cross section of the air flow (a), i.e. by translation movement of the test tube rings (Fig. 7). The temperature gradient is regulated by distance (b). Different temperature gradients in the tubes can be simultaneously regulated using an inclined cooler, i.e. "inclined cold bench". By varying the internal and external cooler shape and dimensions, a family of coolers can be modeled for different intervals of temperature gradients and crystallization rates. Different crystallization fronts and rates in crucible columns can also be regulated below the cooler so that crystallization starts on the surface of the melt (Fig. 8). Crystal growth then occurs downward the lower interface on the floating crystal.

By increasing the air flow velocity, the crystallization front spreads to the other end of the testing tube. The interval of the crystallization rates in each of the testing tubes of the devices (Figs 7, 8) is regulated by the air flow, i.e. the cross section a, which increases or decreases by relocating the moving rings, along with the cooler tubes. The temperature gradient is regulated by distance regulators b (Fig. 7).

Besides the standard case of the "Crystallization bench", other geometric solutions are possible in the design of the part of the devices [10]. Different thermal gradients in test tubes can be simultaneously regulated by the inclined cooler (or some other part of the cooler) relative to the axis of the furnace (Fig. 8). The shape of crystallization fronts and the crystallization rates in the crucibles are regulated by the path and the cross section of the air flow (a) of the cooler, as well as by the distance regulator from the surface of the melted material (b). By such creations and innovations, considering shapes and cooler functioning, the possibility of the Stober method realization in chamber and tube furnaces is accomplished.

The project of the original developed devices, the so called "the moving crystallization bench" (Fig. 10) contains some of the more complex forms of the aerial cooler which is in the shape of a cylindrical tube, which is located in another tube, which can have one or two parts, with a bearing for the Tamman test tubes [11].

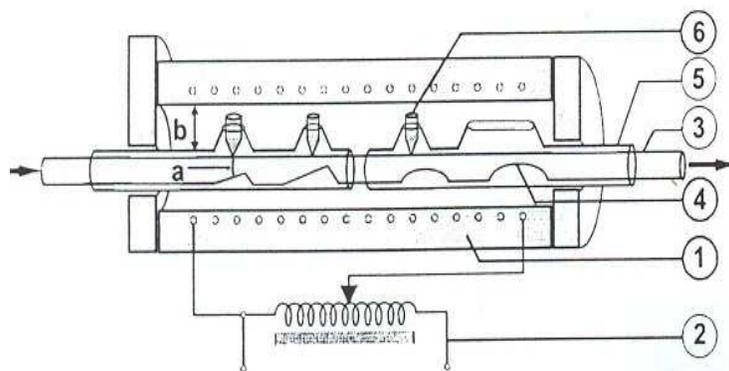


Fig. 10. A tube furnace for obtaining crystals: (1) laboratory tube furnace, (2) continuously changeable transformer, (3) air cooler (telescopic cold bridge), (4) cold "thresholds", (5) cylindrical tube with the mounting holes and grooves (telescopic test sieve) and (6) family group of Tamman test tubes.

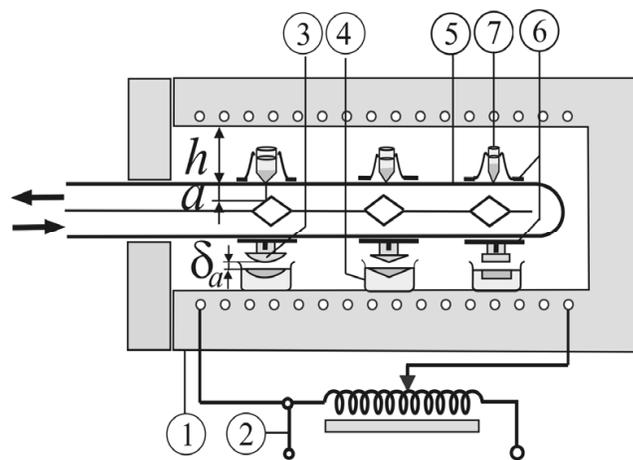


Fig. 11. Apparatus for combining methods: (1) Laboratory chamber furnace, (2) continuously changeable transformer, (3) movable plugs, (4) columns of crucibles, (5) air cooled toothed tube ("crystallization finger"), (6) movable mounting rings, and (7) Tamman test tubes.

The method of testing crystallization, as well as possible variations of the processes are described. The formula for crystallization rates depending on the parameters of the cooler and the characteristics of the material, as well as respective temperature changes. It creates great possibilities for utilization of various crystallization rates.

Tamman's test tubes of various shapes and sizes can be laid out to the moving cylindrical tube (the so-called "sieve"). One can accomplish the simultaneous test of the crystallization for a great number of different Tamman's test tubes. They are of various temperature gradients, intervals of crystallization rates, and materials. They can be used for obtaining single crystals from the melt by using cheap and practical modular devices-crystallization apparatus with the moving elements.

The development of the models of one group of apparatuses, whose work is based on single tube horizontal cooler, has developed in several phases. Each one of the phases is characterized by innovations in the series of details, and therefore a very high level has been achieved. That level has gained a special, important confirmation by publishing the paper with newly accomplished results in the professional journal [12].

In the published article [13], the original modification of the devices, which is considerably more sophisticated and efficient than the previous class of the device. It has been created based on the experience and the series of practical conclusions from the previous models. That article initiated the design of a certain number of devices, which are based on the simultaneous unwinding of the Tamman and Stober methods (Fig. 11). The specially adapted cooler, functional for this purpose, has been installed in the laboratory chamber furnace [13]. The cross section of the fluid current and the distance of the cooler from the surface of the vessel where the melt is located, define the shape of the fronts and the crystallization rates. Some more demanding and economical variations of these devices contain two tube-coolers, for the arm with Tamman's test tubes. The tube which serves as the test tube carrier can be mobile and can contain more than one series of Tamman's test tubes in telescopic test sieves in the previous paper [13], the possibility of simultaneous realizations of Stober and Tamman's methods has been accomplished. The presented solution and the defined modifications, with the aim of improving the conditions of crystallization by these methods can be applied in the tube furnace in the horizontal positions, too. The most sophisticated devices of so called double-tube horizontal models are achieved by flexing one tube by 180 degrees, or two horizontal tubes linked by vertical linking extensions. This is not only focused on accomplishing simultaneous developments of the crystals utilizing the two methods (Tamman's and Stober's), but it is the invention of the quality forms, the positioning of every single test tube, cooler aperture up to the influence on the front crystallization according to certain calculations [14].

The creation of a certain number of functional vertical coolers, which are previously presented, has made the simultaneous realization of the projects with the crystallization devices with vertical coolers possible.

The model of an air cooler, which is vertically positioned in the laboratory crucible furnace (so-called "finger") is presented in the paper [15]. Some bended Tamman's test tubes are positioned on the cooler with the help of rings and sliders of the test tube carrier. The formula of linear crystallization rating in each test tube is derived from using the balance between the latent heat of the solidification and removed heat through the cooler. The possibility of translation of each test tube independently is considered, with the aim of simultaneous probe of the matrices of various crystallization rate intervals.

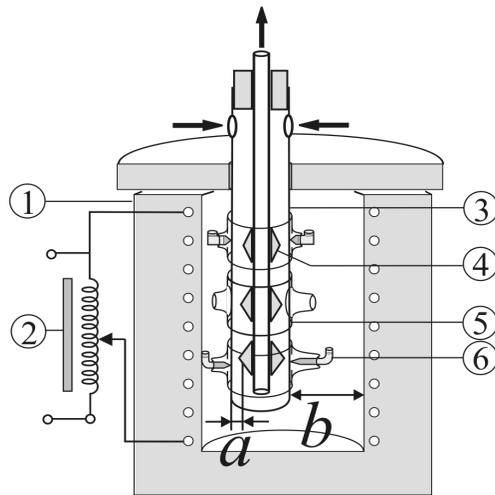


Fig. 12. Multifunction crucibles to obtain crystals: (1) Laboratory crucible furnace, (2) continuously changeable transformer, (3) air cooler ("cold finger"), (4) movable cold "thresholds", (5) movable mounting rings, and (6) curved Tamman test tubes.

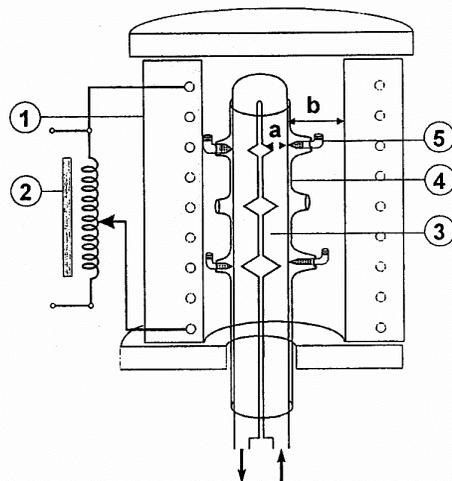


Fig. 13. Apparatus for obtaining crystals: (1) laboratory tube furnace, (2) continuously changeable transformer, (3) air cooler ("cold tree"), (4) movable cylindrical tube with the mounting holes ("test sieve"), (5) family of ("grafted") Tamman's test tubes.

The devices in work [16] present the basis for the previous solution of the new apparatus (Fig. 12), but there is a difference in the flexibility of the elements of the devices in the systems as well with the purpose of the geometrical solution of the test tube (with the melt), with many possibilities of the realization of various temperature gradients.

The devices for the crystallizations shown in Fig. 13 presents exactly one level more operative devices [17] than those shown in Fig. 12. These systems usually consist of aerial coolers (with a cold fluid flowing through) and movable cylindrical tubes with placable holes for Tamman's test tubes. The coolers, in this case, are movable, and they give the possibility of definition of certain parameters during the crystallization process. That is how one can very operatively influence the progression of the process and the quality of the obtained crystal.

The mobile test tube carrier, with the melt, can easily enable an adequate position of the test tube tip, depending on the cross section aerial currents through the cooler. It is easier to control the parameters which influence the substantial magnitudes in the crystallization process (crystallization rate, temperature gradient) that way.

An example of an even higher quality of the devices with vertical coolers (Fig. 12), enable us to translate and move the cooler vertically, but also very convenient for quality work due to the various possibilities of the cooler rotation. It enables the regulation of the front crystallization wanted regulation dynamics, which enables the conditions to obtain quality crystals [18]. These devices have emphasized the mobility of elements, and higher potential for the work by choosing the position of the test tube, and the number of the test tube, in the process of crystallization. It is better than that of the devices in Fig. 13, thanks to the fact that it contains a constructive design solution, with a mobile ring and a mobile mechanism of the test tube carrier.

The achieved variety, considering the design, on the crystallization devices, with another cooler class, has brought a new quality in the sense of the possibility ensure a heightened quantity of the melt. It could be in strictly defined and stabilized conditions, which is substantial as an introductory activity, for the crystallization process itself. Such an idea has been realized and has justification in constructive solutions of the devices which are shown in papers [19] and [20].

The original devices for obtaining single crystals from the melt in coherence with the new demands considering the quantity of the melt, as well as obtaining the possibility where more devices can be put in with melted substances with similar melting points. By variation, those crystals are formed in various ways, depending on the conditions. In this case, the idea of applying the Tamman's method with very specific sets of testing tubes, in a laboratory crucible furnace [19] was realized. The regulation and simultaneous crystallization of several substances for a few nucleations of various temperature gradients and crystallization has been made possible.

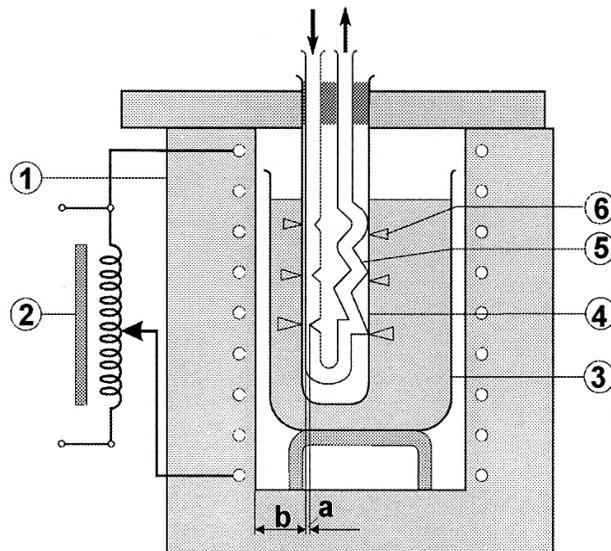


Fig. 14. A crystallization cooler in a crucible furnace. (1) laboratory crucible furnace, (2) continuously changeable transformer, (3) crucible (4) test tube (5) moving air cooler ("cold ear-rings"), and (6) Tamman test tubes.

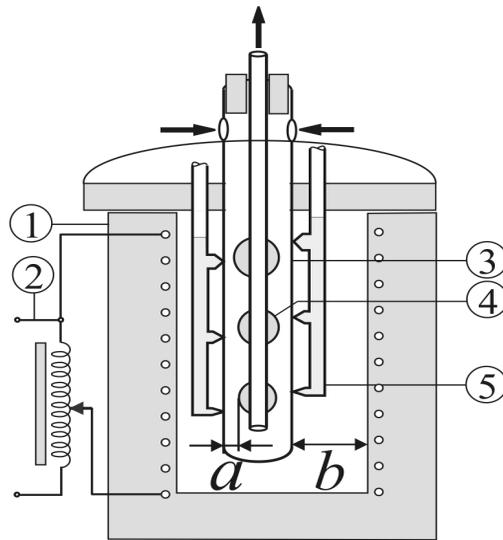


Fig. 15. Crystallization apparatus: (1) laboratory crucible furnace, (2) continuously changeable transformer, (3) air cooler ("cold key"), (4) movable rings and (5) branched Tamman's test tube ("crystallization test comb").

The combination of several Tamman's test tubes in the form shown in Fig. 15 makes the growth of several crystal from the melt possible, as well as obtaining the conditions for several devices with melted substances who have approximately the same melting points. By variation of the shape and the size of the cooler (inside and out), can model a family of "cold keys" for testing a wider interval of temperature gradients and crystallization rates.

The fusion of the best performance of the devices shown in Figs 12, 13, 15 has benefited the crystallization process in the new devices [14] with a vertical cooler in the crucible furnace, chamber furnace or tube furnace. They also come with a modern form, better functioning and higher economic value, and other important traits which have been greatly improved. Controlled functioning of certain phases during the crystallization process with great reliability for obtaining the crystal's wanted characteristics.

The devices who improve the efficient solution of the form of the apparatus related to the previously described apparatus [21] are shown in Fig. 14 (from the constructional point of view, they are very similar at the first glance). The presence of a larger quantity of the melted substance, but also a bigger number of the test tubes for obtaining adequate crystals with big potential for variation of the conditions, which are very important for the regulation of the crystallization rate, is made possible [22].

3.1 New generation of devices for crystal growth – "Expert systems"

Before mentioned division of coolers on horizontal and vertical ones, and related construction of apparatus could not exist within the given frame. Rich experience in connection with work on crystallization apparatus and vision of development directed towards new possibilities, led to so called "hybrid" solutions for the coolers. In their regime of work, they employ both horizontal and vertical fluid flow.

This, in turn, gives a variety of opportunities for development of original, high quality devices with new possibilities and advantages for crystallization process. A increased efficiency and reduced costs may also be expected.

In [23] a successful realization of combined (“hybrid”) device is demonstrated in laboratory chamber furnace. For that purpose, one improved model of crystallization cooler in ladder-like shape on which movable bended Tamman’s test tubes are positioned, is presented. By finding the appropriate angle between axes of the test tube and direction of crystallization, defect drainage towards test tube wall may be regulated. To this intermediate group of crystallization devices belongs the apparatus described in [24].

It is quite obvious that fluid current that conducts crystallization heat from a certain level of test tubes, circulates several levels by passing through profiled sections. Therefore, on the remaining semicircular levels, we may, either have the same substance with different cooler cross section on the location of the test tube (in this way we will get the family of crystals of same substance), or, on each level we may have a system of test tubes of different substances from a group of substances having more or less the same crystallization conditions.

In [10], [13] and [25], original modification of devices based on the Stober’s method are presented. During the research of methods for crystallization regulation in laboratory chamber furnace for crystal substances with unknown crystallization parameters, we reached the conclusion that combined Tamman-Stober’s method can be employed.

Particularly adapted cooler for this purpose was installed in laboratory chamber furnace [26]. The forms of crystallization fronts and crystallization rate in crucibles are regulated via trajectory and the cross section of cooler air flow (d_1), and via the distance of the cooler from the furnace wall (d_2). In more demanding and more economical type of this apparatus, two pipe coolers can contain an array of Tamman’s test tubes on one branch [27].

The apparatus presented in [28] is practical realization of combination of more elements from different types of presented devices. It is specific in the sense that it has built in parts of devices that contain several groups of Tamman’s test tubes of different shapes, volume and inclination of test tube axes where the formation of crystals is expected. It more complex variant, the apparatus may contain ensembles of coolers and test tubes. In that way, many of the steps can be repeated within single crystallization process [29]. During the research on realization of monocrystals of family of substances with unknown crystallization parameters in laboratory chamber furnace, we have modeled air cooler that enables simultaneous crystallization of several substances at different temperature gradient, shapes of crystallization fronts and crystallization speeds in column of crucibles and test tubes.

By upgrading the existing experiences and improving the characteristics of previously described classes of devices, we have achieved results which give a solid bases for accomplishing the highest goal set during production of new devices for crystal growth from the melt: realization of “smart systems” that control process of crystal growth via computer programming [30].

The first results appeared almost simultaneously in two articles: in Russian journal *Instruments and Experimental Techniques* [31] (Fig. 16), and another one in American journal *American Laboratory* [32] (Fig. 17), both published in 2011.

This new class of devices (“superclass”) owes its name to its multifunctionality, and ability of its dynamical elements to react almost instantaneously to the tasks regarding regulation and monitoring the crystal growth. It is achieved by establishing permanent connection of devices with computer-controlled programs [33]. At this stage of realization, results of process simulation and apparatus conditions are used. Nevertheless, practical realization of establishing direct connection of computer to apparatus and its movable parts (cooler and test tubes with melt) is a matter of time.

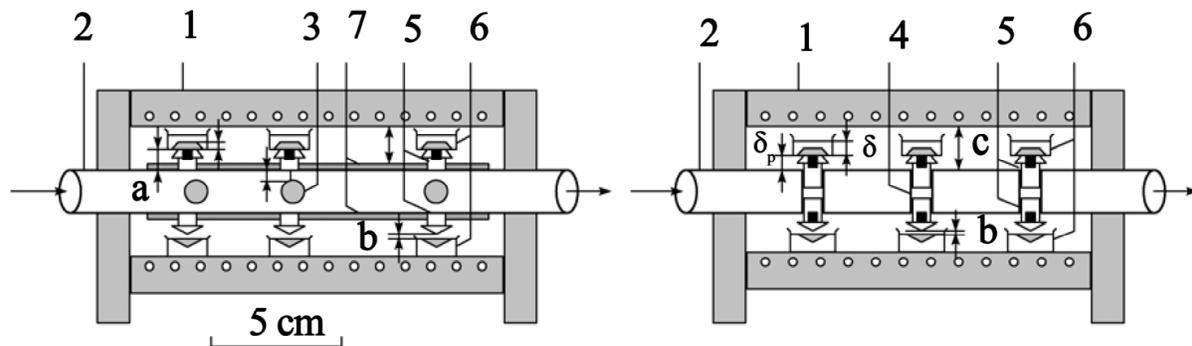


Fig. 16. "Programmed crystallization bench" for crystal growth from melt: (1) laboratory tube furnace, (2) air cooled tube ("crystallization shelf-comb"), (3) radial holes in a horizontal position ("crystallization thresholds"), (4) radial holes in a vertical position ("crystallization sockets"), (5) movable cold plugs, (6) columns of crucibles, and (7) slide bars.

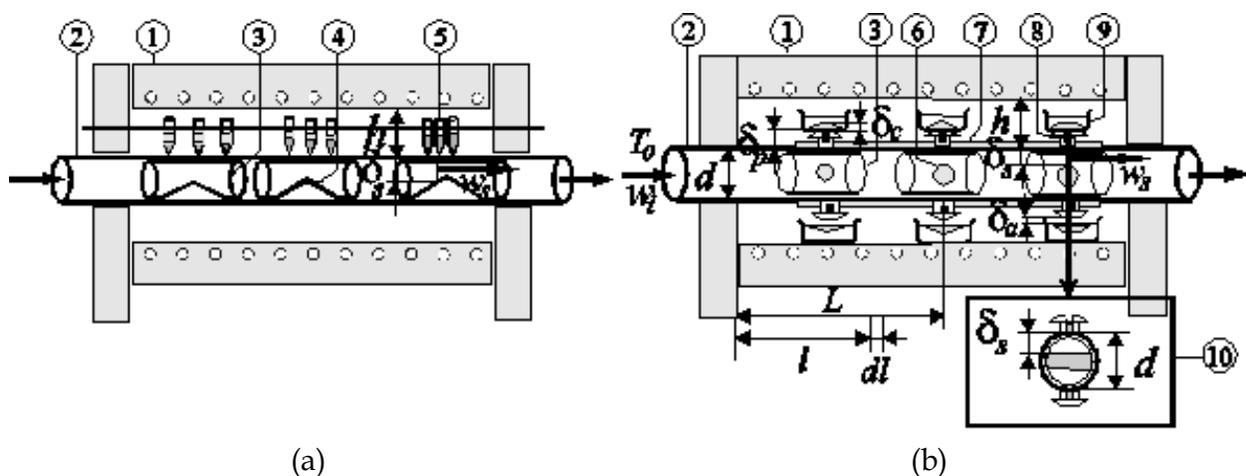


Fig. 17. "Smart" coolers for the combined methods of crystal growth from melt: (modular unilateral (a), and bilateral (b) "crystallization comb" in a tube furnace). (1) laboratory tube furnace, (2) air-cooled tube, (3) modular and movable pipes: (4) "Δ" cold thresholds, (5) string of family group of Tamman test tubes, (6) radial holes in a horizontal (or vertical) position ("O" or "I" cold thresholds), (7) slide bars (or movable mounting rings), (8) movable plugs with modular heads, and (9) column of crucibles; (10) cross section of the cooler.

Programmed conditions will be controlled by computer system that directly define the dynamics of movable systems, such as optimal positioning of cooler within the furnace, controlled heat dissipation in the course of crystallization as well as monitoring the position of test tube carriers where crystallization from the melt is taking place.

4. Results of modeling

The rate of melt solidification depends upon extracting the latent heat of solidification. For a time interval t a crystal layer of thickness δ_c is formed (Fig.17). During the formation of an elementary crystal layer of thickness $d\delta_c$ per unit area, the amount of heat released is

$\lambda\rho d\delta_c$ (λ denotes the latent heat of solidification and ρ the crystal density); the latter is being extracted through the cooler for a time interval dt . On this basis the following equation may be written [34].

$$\lambda\rho d\delta_c = \frac{\Delta T(L)}{1/\alpha_s + \delta_p/k_p + \delta_a/k_a + \delta_c/k_c} dt \quad (1)$$

where $\Delta T(L)$ denotes the difference between the temperature of the melt and that of the air stream; α_s is the coefficient of heat transfer from the cooler wall to the air stream; and k_p , k_a and k_c designates the heat conductivity of the plug, air and crystal respectively (Fig. 17b). Transforming equation (1) we obtain

$$R = \frac{d\delta_c}{dt} = \frac{\Delta T(L)}{\lambda\rho(1/\alpha_s + \delta_p/k_p + \delta_a/k_a + \delta_c/k_c)} \quad (2)$$

The quotient $d\delta_c/dt$ denotes the rate of crystal layer growth which is usually represented by the symbol R .

The coefficient of heat transfer from the cooler wall to the air stream can be calculated using the following expression [35]:

$$\alpha_s = \left[4,13 + 0,23 \frac{t}{100} - 0,0077 \left(\frac{t}{100} \right)^2 \right] \left(\frac{U}{4A} \right)^{0,25} (w_{s0})^{0,75} \quad (3)$$

where t is average temperature of the air stream in $^{\circ}\text{C}$ (up to 1000°C), U and A are circumference and area of the cross section of the airstream, respectively – see (10) in Fig. 17b,

$$w_{s0} = w_s \left(\frac{273}{273 + t} \right),$$

w_s is average velocity of the airstream (0°C , 1.013 bar) in m/s.

On the basis of the continuity of the airstream, and the cross section at the entrance of the tube and on the threshold – see (10) in Fig. 17b, the following expression for the velocity of the air stream on the threshold w_s we have derived:

$$w_s = w_i \left(\frac{\pi}{\varphi - \sin \varphi} \right) \quad (4)$$

where w_i denotes an average velocity of the air stream at the entrance of the tube

$$\varphi = 2 \arccos \left(1 - \frac{2\delta_s}{d} \right)$$

in rad, δ_s is the width of the air stream, d is diameter of the tube (Fig. 17b).

Based on the fact that the heat removed from the cooler wall is equal to the heat accepted by the air stream, we have derived the following expression (integral equation) for the difference of the temperature between of the melt and that of the air stream along the cooler $\Delta T(L)$:

$$\Delta T(L) = \Delta T_0 - \frac{4}{d} \int_0^L \frac{\alpha_s \Delta T(l)}{\rho_a c_a} dl \quad (5)$$

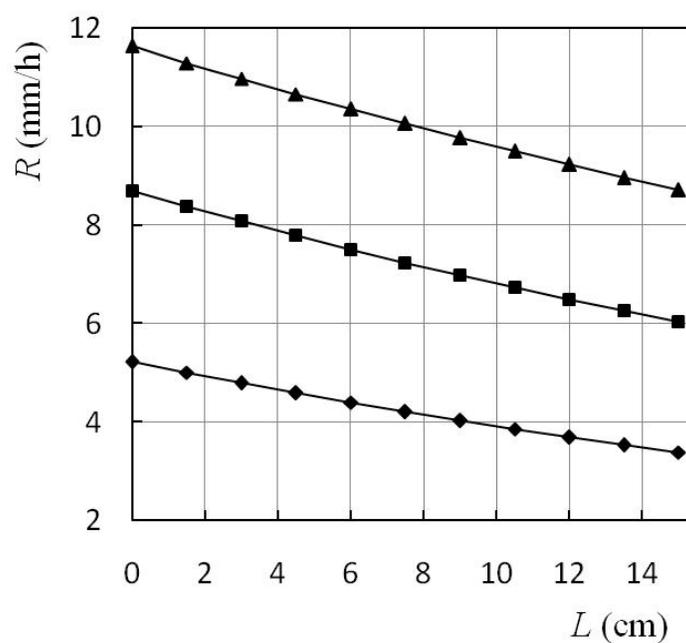
where ΔT_0 denotes the difference between the temperature of the melt and that of the air stream at the point $L=0$ (at the entrance of the tube), d is diameter of the tube, α_s is the coefficient of heat transfer from the cooler wall to the air stream - eq. (2), when put

$$\left(\frac{U}{4A}\right) = \left(\frac{1}{d}\right)$$

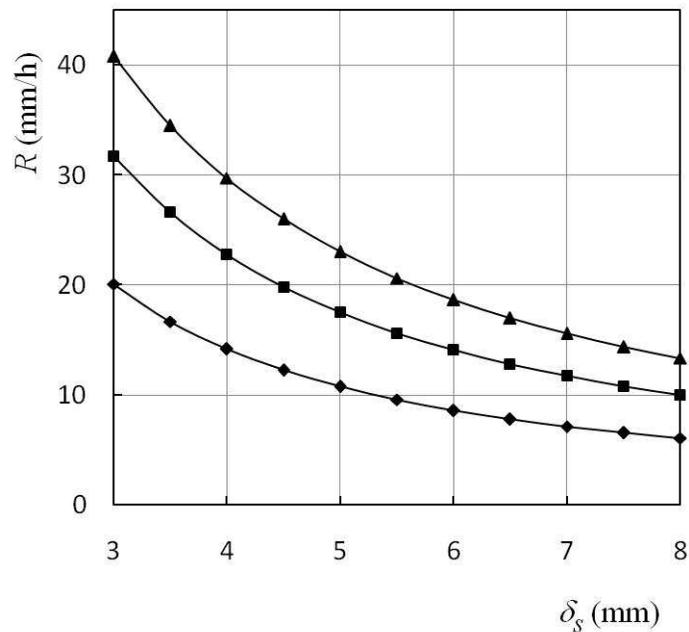
(i.e. tube without thresholds), $\Delta T(l)$ denotes the difference between the temperature of the melt and that of the air stream at the point l (Fig. 17b), ρ_a designates the air density, c_a is heat capacity of the air.

The crystallization parameters (designed in Fig. 17b) are determined by the numerical analysis of eqs. (2), (3), (4) and (5), in the case of bismuth: $T_{melt} = 271$ °C, $\lambda = 52300$ J/kg, $\rho = 9800$ kg/m³, and $k_c = 7.2$ W/mK, In all numerical calculation is was taken that: $k_p = 0.756$ W/mK (pyrex i.e. borosilicate glass, softening point ≈ 600 °C), $k_a = 0.0342$ W/mK, $\rho_a = 0.682$ kg/m³, $c_a = 1.035$ kJ/kgK, $\Delta T_0 = 251$ °C, $T_0 = 22$ °C (the temperature at the entrance of the tube), $d = 2$ cm, $\delta_p = 5$ mm, $\delta_c = 0$ mm (on the bottom or the surface of the melt).

The dependence of the crystallization rate R on the position of the plug along the cooler L is represented on Fig. 18a, when $w_s = w_i$, eq. (3), i.e. the tube without the thresholds. As can be seen from Fig. 18a, the crystallization rate decreases with increasing L , which is the consequence of the fact that ΔT decreases with the increase of the L , eq. (5). Fig. 18b shows the dependence of the crystallization rate R on the with of the air stream δ_s - see (10) in Fig. 17b. As can be seen from Fig. 18b, the crystallization rate increases with decreasing δ_s , which is the consequence of the fact that w_s , eq. (4), and consequently α_s , eq. (3) and R , eq. (2) increases with decrease δ_s .



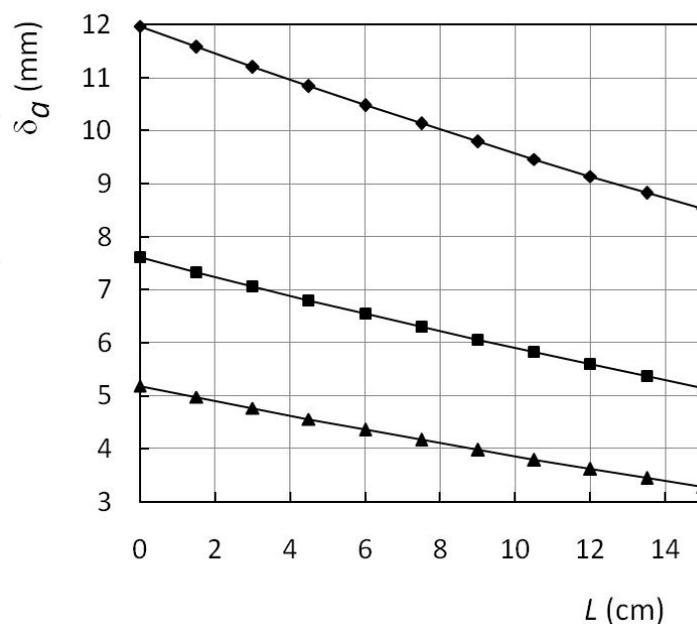
(a)



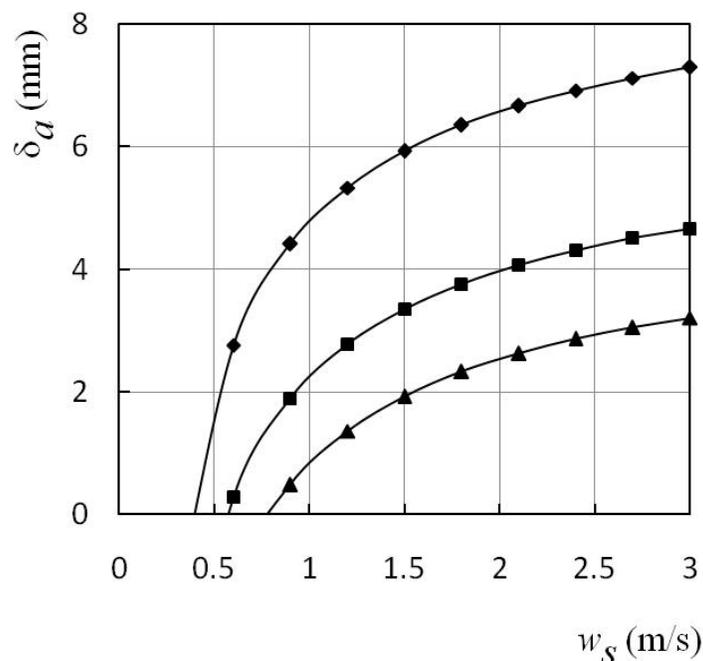
(b)

Fig. 18. Crystallization rate R as a function of the position of the plug along the cooler L , and the width of the air stream δ_s , respectively, when: $-\diamond-$ $w_i = 0.3$ m/s, $-\square-$ $w_i = 0.6$ m/s, $-\triangle-$ $w_i = 0.9$ m/s; $\delta_a = 0$ (crucibles above the plugs) (a) $\delta_s = d$; (b) $L = 9$ cm (Fig. 17).

Fig. 19a represent the possible values of distances of the plug head from the surface of the melt δ_a and the position of the plug along the cooler L , for definite values of crystallization rates. As can be seen, if L is larger, then δ_a must be smaller for the definite crystallization rate, which is the consequence of the fact that ΔT decreases with increasing of the L , - eq. (5) and R increases with decreasing δ_a - eqs. (2), (3) and (4).



(a)



(b)

Fig. 19. Dependence of the distances of the plug head from the surface of the melt δ_a (crucibles below the plugs, Fig. 17b) on the positions of the plug along the cooler L , and the velocities of the air stream w_s respectively, for the crystallization rates $-\diamond-$ $R = 5$ mm/h, $-\square-$ $R = 7$ mm/h, $-\triangle-$ $R = 9$ mm/h, when: (a) $w_s = 2.4$ m/s; (b) $L = 7$ cm.

In Fig. 19b the possible values of distances of the plug head from the surface of the melt δ_a and velocities of the airstream w_s are presented, for definite values of crystallization rates. As can be seen from Fig. 19b, if w_s is larger then δ_a must be larger for the same crystallization rate, which is the consequence of the fact that α_s increases with increasing of the w_s - eq. (2), and R decreases with increasing δ_a - eq. (1)

5. Conclusion

The subject of our research belongs to the field of crystal growth from the melt, particularly growth conditions depending on the design and construction of crystallization apparatus, which have significant influence on germ formation conditions and controlled crystal growth. A class of new modern devices for crystal growth from the melt, based on the well-known methods and crystal growth techniques, is presented in the paper. Crystal growth from the melt plays an important role in area of electronic technologies, because it includes a major part of most efficient methods for production of semiconductor and electronic monocrystal materials. In this monograph, we have systematically presented results concerning crystal growth from the melt, from both renowned authors and the author of monograph.

Technology of crystal growth depends on apparatus state-of-the-art and on devices with specific characteristics for particular growth method. However, in order to meet specific demands in their subsequent application, some of the apparatus for production of standard materials have additional peculiarities. Consequently, an upgrade in both constructional and functional sense for a variety of apparatus for crystal growth from the melt was

necessary. As presented in the paper, this resulted in development of a class of novel devices with notably improved solutions for both some elements of the device and device as a whole.

Basic settings for the new approach in fulfilling desired crystal growth conditions and flexibility of specific devices while varying some parameters, were obtained through realization of whole set of coolers, starting from elementary specifically positioned to the, so called, mobile coolers of different profiles.

Studying of conditionality of crystallization parameters and physical conditions of the process itself, generated an original idea where modern design coolers gain multifunctional role. On the one side, they have become carriers of the ensemble of test tubes with melt, and on the other side they allow for the positioning of melt in desired spots thereby bringing about the needed temperature gradient. Finally, cooler-melt system has a potential of easily being positioned where necessary by moving it in various directions or by rotating it within the space available in furnace. A particular quality in innovations that we came upon, is that idea of multifunctional coolers triggered an idea of incorporating computer system into the crystallization process. Application of computer systems allows one to define crystallization conditions prior to the crystal growth via simulation process. In addition, it is possible to permanently control and monitor quality of crystallization process. Development of some original programs in MATH LAB only confirmed validity of idea. This gives vast opportunities in presented modern approach to growth of crystals and monocrystals.

All the mentioned innovations in both specific parts of crystal growth apparatus and apparatus as a whole, allowed relatively easy reproducibility of crystallization process. This approach enables, for the predefined conditions, simultaneous growth of a family of crystals of single material in same or different conditions on the one side, and simultaneous growth of different material crystals in, more or less, same crystallization conditions on the other side. Along with the described multifunctionality, a new class of crystal growth devices gained in quality and importance in connection with low cost, efficiency, rationalization and modernization of crystallization process. Usage of computer modeling and development of original computer programs are a good basics for achieving the highest goals of this monograph: to incorporate, via application of information technology in the process of crystal growth from the melt (with the use of latest class of devices designed for crystal growth), in a certain way, the expert systems. In this way, efficiency and accuracy is significantly increased due to a possibility of controlling and simultaneously eliminating undesired effects, in a process that is almost fully automatic and that can be influenced essentially in order to get a crystal of desired quality. Results presented here are of great practical interest for theoretical and applied research in solid state physics, as well as in the area of new materials, all this fulfilling high requirements and standards demanded in both laboratory and industry growth of crystals and single crystals.

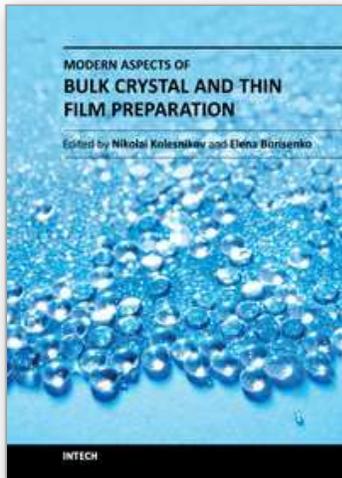
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In modern research and development, materials manufacturing crystal growth is known as a way to solve a wide range of technological tasks in the fabrication of materials with preset properties. This book allows a reader to gain insight into selected aspects of the field, including growth of bulk inorganic crystals, preparation of thin films, low-dimensional structures, crystallization of proteins, and other organic compounds.

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